The Relevance of Fuel Ethanol Utilization to Urban PAN

By

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Fuel ethanol should not have a significant impact on the urban oxidant peroxyacetyl nitrate (PAN). At high concentrations PAN is a powerful oxidant, lacrymator, phytotoxin, and precursor to ground-level ozone (Gaffney et al., 1989, and Stephens, 1969), but the levels of PAN recently observed are much lower than were seen a couple of decades ago. There have been no air quality standards for PAN since 1977, when a total oxidant smog standard (that could include PAN) was replaced with an ozone-only standard.

Acetaldehyde is well known as one of the many precursors found in the urban mixture of organic compounds that lead to PAN and ozone formation. Acetaldehyde is the major secondary product of ethanol itself in the atmosphere or from its use as a fuel in internal combustion engines. Because of PAN's role in smog formation and its potential health and ecological effects, the potential impact of oxygenated and/or reformulated motor vehicle fuels – in particular, fuels containing ethanol – on atmospheric levels of PAN is of concern to some scientists (UC Davis, 1998). Thus, it is certainly logical and reasonable to consider that the use of fuel ethanol might exacerbate any pollution problems associated with PAN. However, it is also important first to consider the relevance of PAN to current urban smog problems and second to quantify the interrelated roles of PAN, acetaldehyde, and ethanol in typical urban atmospheres.

How important is PAN?

Early studies of air pollution noted that PAN at levels of 100 ppb for periods of 5 hours could cause moderate plant damage to crops such as young pinto beans or even severe damage to flowers such as petunias (Darley et al., 1959). At high concentrations PAN could also be important to urban ozone because it serves as a reservoir for nitrogen oxides and hydrogen-containing free radicals. As such a reservoir it might also play a role in the transport of smog from urban to rural areas. It has been cited as a significant reservoir for nitrogen oxides in the global troposphere (Singh and Hanst, 1981).

MacKenzie (1984) noted that "some people are sensitive to PAN at concentrations of about 10 [ppb] …[but] most people don't notice any effect until concentrations reach 50 [ppb]." Grosjean et al. (1995) note that PAN levels in the South Coast Air Basin (SoCAB) reached maximum concentrations of 9.9 ppb during 1994.   Such concentrations are considerably lower than earlier in the South Coast Air Basin; Altshuller (1983) notes that levels as high as 70 ppb had been observed there over thirty years ago. Hence, the levels of PAN recently observed are much lower than were seen a

couple of decades ago, even though PAN has not directly been part of any air pollution control program since 1977. It should also be noted, that routine measurements of PAN are not available as a further consequence of the ozone-only standard since 1977.

While maximum levels of PAN have been reduced from 70 ppb to below 10 ppb during the past thirty years (a factor of 7), the highest ozone concentrations during this time have been reduced from approximately 500 ppb down to the range of 250 ppb (only a factor of 2). That is, PAN concentrations have decreased proportionally much more than ozone as precursor emissions were reduced. Whitten et al. (1980) showed how PAN simulated in photochemical models can change more than linearly with precursor loading, while ozone varies less than linearly. Thus, as urban emissions were controlled to successfully cut urban ozone in half, these same controls reduced PAN proportionately much more. Furthermore, future emissions controls should be able to continue reducing PAN proportionately more than ozone because ozone reductions will be influenced more by the relatively high natural background level of ozone in the free troposphere. The tropospheric background level of PAN (less than 0.1 ppb) is a factor of one hundred below current maxima; while ozone in the free (i.e., unpolluted) global troposphere (near 30 ppb) is less than a factor of three below the new 80 ppb standard.

How important is acetaldehyde to PAN formation?

Altshuller (1993) notes that many volatile organic compounds (VOC) are precursors to PAN formation, most notably aromatic compounds such as xylenes and tri-methylbenzenes. Aromatic VOC's without an ethyl moiety are not known to even produce acetaldehyde. Acetaldehyde is not a necessary precursor to PAN formation, since the peroxyacetyl radical that is required to form PAN, can be generated from such species as methylglyoxal or biacetyl, and these species have been identified as intermediates during the smog-forming photochemical oxidation of aromatics such as toluene, xylenes, and tri-methylbenzenes.

Guthrie et al. (1997) estimate (based on SCAQMD, 1994, and Fieber et al., 1994) that pure acetaldehyde emissions account for less than 0.2 percent of the 1987 anthropogenic organic emissions in Los Angeles. Because the on-road mobile acetaldehyde emissions are approximately two-thirds of the anthropogenic total, the mobile acetaldehyde is only about 0.1 percent of the total inventory. Similarly, Guthrie et al. (1997) estimate (based on Morris et al., 1994) that on-road mobile emissions of acetaldehyde for Baltimore in 1988 are about 0.08 percent of the total anthropogenic organic emissions. More recent data are consistent with such low emissions of pure acetaldehyde from vehicle exhaust. The California Air Resources Board (CARB, 1998) tested 12 vehicles with California Cleaner Burning Gasoline (CBG) made with MTBE and these data show 0.5 percent acetaldehyde in the exhaust emissions. A recent inventory (SCAQMD, 1997) shows that gasoline-vehicle exhaust for the year 2000 is 62 percent of the total mobile emissions and mobile emissions are 35 percent of the total VOC emissions. Combining 0.5 percent acetaldehyde in exhaust with these percentages

for the year 2000 leads to a mobile-related pure acetaldehyde emissions level of 0.1 percent using MTBE fuel. While there are several studies showing that acetaldehyde from vehicle exhaust appears to be in the range of 0.1 percent of total VOC emissions, it should be noted that not all VOC's generate PAN equally.

Ligocki and Whitten (1992) developed a version of the Carbon Bond IV (Gery et al., 1989) that explicitly treats pure acetaldehyde and PAN. Using typical urban mixtures and the Ligocki and Whitten version of smog chemistry in photochemical models shows that 1 percent of total VOC emissions as acetaldehyde contributes approximately 8 percent to PAN concentrations when PAN is near 10 ppb and ozone near 250 ppb. Emissions of aromatics generally account for the majority of PAN precursor VOC's in these simulations. Thus, 0.1 percent acetaldehyde emissions are estimated to contribute less than 1 percent to ambient PAN concentrations.

It should also be noted that Kirchstetter et al. (1996) report about a 25 percent reduction in aromatic VOC's in tunnel data attributable to the introduction of oxygenated fuel. Such reductions in aromatics are expected when high octane oxygenates (e.g., methyl *tertiary*-butyl ether, [MTBE] or ethanol) are mandated to abate CO emissions; aromatics have been the most common gasoline component refineries use to meet octane specifications. Hence, there is reason to believe that the use of oxygenates such as ethanol would actually decrease some PAN precursors, most notably those stemming from the high octane aromatic compounds that would be reduced most often to maintain overall octane.

How important is ethanol to PAN formation?

If ethanol replaces MTBE in gasoline, there is first the issue of how much acetaldehyde might increase due to the combustion of ethanol, and second the issue of PAN generation from emissions of ethanol itself. As noted above, as ethanol reacts in the atmosphere acetaldehyde is a principal secondary product. The Ligocki and Whitten (1994) version of Carbon Bond smog chemistry also treats ethanol explicitly. Similar tests to those noted above for acetaldehyde show that 1 percent of total VOC emissions as ethanol contributes about 2.5 percent to PAN concentrations when PAN is near 10 ppb and ozone near 250 ppb. Thus, ethanol itself can lead to PAN, though not as efficiently as direct emissions of acetaldehyde.

Mayotte et al. (1994) of the U.S. EPA found a 140 percent increase in acetaldehyde emissions in a 34-vehicle fleet using a reformulated gasoline containing 10 percent ethanol compared to using a similar gasoline made with 11 percent MTBE. Recently the California Air Resources Board released the results of a 12-vehicle test program that compared a typical California Cleaner Burning Gasoline (CBG) made with 11 percent MTBE to the same fuel made with 10 percent ethanol instead. These new data are similar to the EPA tests reported by Mayotte et al. (1994). The new California tests show an average increase in acetaldehyde of 160 percent for the 12-vehicle fleet.

However, such percentage increases in acetaldehyde exhaust emissions would apply to the low base values discussed above. Hence, the contribution to PAN from acetaldehyde exhaust emissions would increase from only about 1 percent to less than 3 percent of total PAN.

While acetaldehyde emissions stem exclusively from exhaust, ethanol can be emitted from both exhaust and evaporative sources. Analysis of the recent 12-vehicle tests (CARB, 1998) using a 10 percent ethanol gasoline blend indicate that average starting exhaust emissions contain approximately 6.6 percent ethanol, but stabilized or running exhaust emissions contain only about 0.6 percent ethanol. Since the ARB (CARB, 1998) estimates that 55 percent of total exhaust emissions are starting exhaust, the average overall exhaust VOC appears to be about 4 percent as ethanol.

The 12-vehicle tests (CARB, 1998) using a 10 percent ethanol gasoline indicate that hot soak evaporative emissions could be 33 percent ethanol on average, while diurnal evaporative emissions could be 14 percent on average. Using the inventory developed by SCAQMD (1997) and running evaporative emissions speciated the same as hot soak emissions (CARB, 1998), the average ethanol content of all evaporative emissions would be 14 percent.

For the overall VOC inventory for the year 2000, an estimate of 2.7 percent ethanol can be obtained by using the SCAQMD (1997) estimates as used above for acetaldehyde (i.e., 62 percent of mobile as exhaust with 4 percent ethanol and 35 percent of total VOC as non-exhaust with 14 percent ethanol). The modeling result of a 2.5 percent increase in PAN per 1 percent in total VOC then implies about a 7 percent increase in PAN for a 2.7 percent increase in VOC as ethanol. This would add to the PAN increase from acetaldehyde related to ethanol use to give a total increase in PAN of 10 percent.

Summary

While it may still be important to consider PAN, current data show that successful emissions controls directed at ozone abatement have apparently been far more effective in reducing ambient PAN concentrations. Moreover, there are reasons to expect that PAN will continue to be reduced proportionately more than ozone in the future. Secondly, the contribution of on-road acetaldehyde emissions (with no ethanol fuel utilization) to urban PAN appears to be on the order of 1 percent. A switch from 100 percent MTBE use in California CBG to full use of ethanol might increase mobile acetaldehyde emissions by approximately 150 percent, which would imply an increase of less than 3 percent in PAN (from ethanol-related acetaldehyde). Even though ethanol itself is less efficient than acetaldehyde as a PAN precursor, the estimated potential 2.7 percent contribution to total VOC from ethanol itself could increase PAN an additional 7 percent. Thus, the estimated total increase in PAN from ethanol use is 10 percent. If current maximum PAN concentrations are assumed to still be as high as 10 ppb, then a

switch from 100 percent MTBE use in California CBG to full use of ethanol might increase maximum PAN concentrations from 10 ppb to 11 ppb.

It would be difficult to observe a small increase in PAN. There have been several studies noting the difficulty of using ambient data to demonstrate any changes associated with fuel reformulation (see for example Rhudy et al., 1995 or Wolfe et al., 1994). The main source of difficulty appears to come from meteorological fluctuations that often lead to larger changes in ambient concentration than any of the changes expected to occur from fuel reformulation. Glen, et al. (1996) show that the widest differences in ambient concentrations due to meteorological effects occurs between summer and winter. These studies mainly concerned the relatively inert pollutant carbon monoxide. Nevertheless, Gaffney et al. (1997) did attempt to connect winter PAN observations to ethanol use. However, Whitten (1998) who claims that Gaffney et al. failed to account for differences in photochemistry between summer and winter meteorology has criticized this paper.

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Wolfe, P., L.G. Anderson, J.A. Lanning, and R.H. Jones (1994) "A structural time series assessment of the effectiveness of the oxygenated fuel program in reducing carbon monoxide concentrations in five western U.S. cities" presented at Air and Waste Management Association 87th Annual Meeting, Cincinnati, OH, Paper 94-WP91.04. hows that the methane fraction is inversely related to the THC emissions. As discussed above the new ARB test fleet represents the lowest 10 percent of the overall emissions. Therefore, the overall inventory (which covers the entire range of emitters) must have a lower fraction of methane. Furthermore, there is compensation (or more) for the remaining methane due to the fact that exhaust NMOG contains some oxygenated intermediate combustion products such as carbonyls (i.e. aldehydes and ketones) that would not be included in THC. Hence, the ratio of NMOG to THC in the original exhaust emissions inventory must have been much closer to unity (if not even slightly greater than unity) than the (less than unity) values seen in the new test data.

Second the evaporative emissions of the test fleet had approximately 11 percent MTBE (an organic counted in NMOG but not a hydrocarbon so not counted in THC), while some of the data used to construct the inventory came from fuels without oxygenates. Data from the Auto/Oil Air Quality Improvement Research Program have previously shown that using MTBE up to 15 percent in the fuel does not significantly change evaporative (NMOG) mass emissions compared to clear gasolines at the same RVP (e.g., see SAE Paper No. 920323). By definition there can be no difference between THC and NMOG with clear gasolines in evaporative emissions. If the traditional ARB emissions inventories were constructed using THC (presumably based on some clear gasolines), then for the newer oxygenated fuels, it could be argued that NMOG should be the better metric for mass evaporative emissions.

The significant differences between THC and NMOG seen in the new data (and presumably not seen in the inventories) adds an artifact that conflicts with the reason why the inventory information is needed (to relate the exhaust to the evaporative mass emissions). It seems implausible that the ARB believes that the "surrogate NMOG inventory" constructed from the new data can be an accurate representation of the NMOG inventory (comparable to the existing THC inventory) that might have been constructed had the data been available.

Contribution of CO to OFPCO

In his peer review Dr. Lucas introduces the section on calculating emissions changes by noting that "The calculation of the ozone forming potential [OFP] which includes the effect of changing CO levels is a complicated procedure." The way the ARB approaches such calculations (that Dr. Lucas supports) is quite complicated but it need not be so

complicated. The ARB methodology requires a careful meshing of two emissions inventories (THC and CO) along with ozone-forming maximum incremental reactivity (MIR) factors and the test data to estimate OFP with CO. The SAI procedure uses the exhaust CO data directly rather than bringing in another inventory. The scientific rule of Occam's razor requires that the simplest of competing theories be preferred to the more complex.

The ARB estimates OFP by using the MIR for some 205 different NMOG species identified in the exhaust emissions. The grams per mile observed for each species is multiplied times its appropriate MIR value to give the grams per mile of potential ozone for that species coming out of the tailpipe. Carbon monoxide also forms ozone as if it were an NMOG specie and CO has an MIR value. It is very simple and straightforward to treat CO as the 206th specie as is done in the SAI method. Then the potential OFPCO out the tailpipe is merely the sum of these 206 products (MIR times grams per mile per species).

In the ARB method OFP is first calculated for the 205 NMOG species (i.e. without CO). Then the relative amount of CO to the "surrogate inventory" constructed for NMOG is estimated based on the separate inventories of THC and CO. Finally, the relative amount of potential ozone from this "inventory" CO (rather than actual test data CO) to the exhaust test data OFP is used to construct a relative value of exhaust OFPCO that can then be related to the OFP for evaporative emissions. The word "relative" is used here to simplify the present discussion. In reality, the ARB uses a complicated series of weighting factors constructed to relate the various emissions impacts of ethanol. In the SAI method the necessary weighting factors for OFPCO are constructed using only one inventory (THC or NMOG). The two methods differ significantly because the CO seen in the new test data is significantly greater relative to NMOG than seen in the ARB emissions inventory so that more "weight" is attributed to the CO-reduction impact of ethanol. Philosophically, the two methods differ on how much the new data can be related to real-world emissions.